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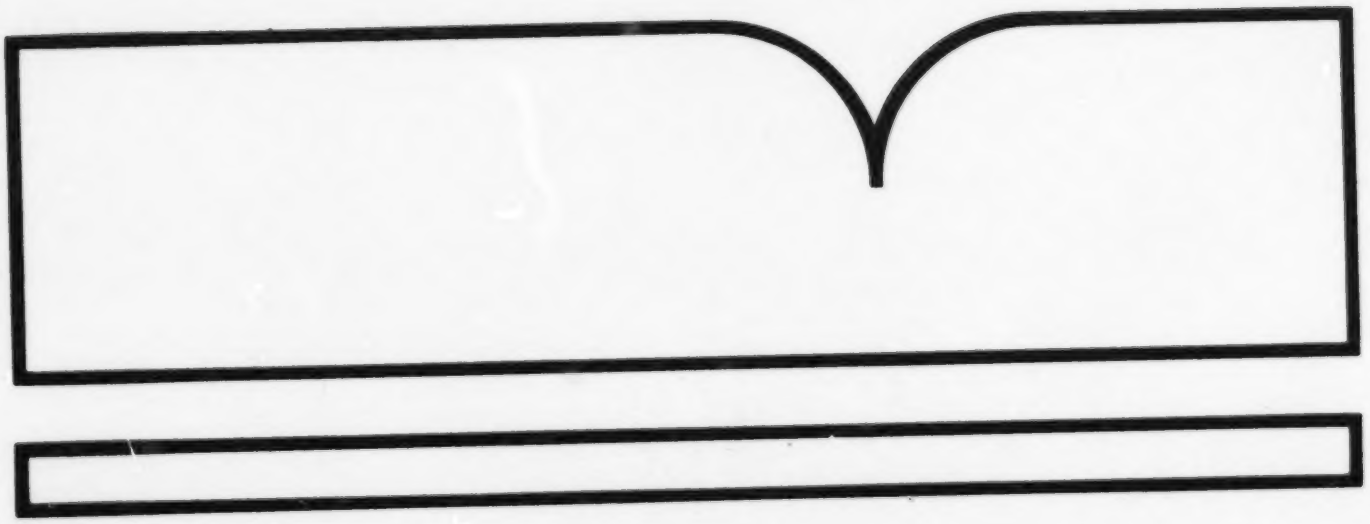

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16. ABSTRACT

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Simulation of Electron Impact Mass Spectra by Charge Exchange in Chemical Ionization Mass Spectrometry

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Chemical ionization (CI) conditions were developed for obtaining mass spectra which bear a striking resemblance to electron impact (EI) spectra. The method, which employs charge exchange reactions in a high-pressure source, is applied to the identification of priority pollutants. In most cases identification of the compounds by using computer-generated searches of the pseudo-EI spectra against libraries of true EI spectra was possible with confidence levels of 80% or greater.

Mass spectral surveys for the characterization of samples are most efficiently accomplished by using computer-generated library search routines for the identification of unknowns. Since the only libraries of spectra commonly available contain mass spectra obtained under electron impact (EI) conditions, such searches are usually carried out on EI mass spectra of unknowns. For laboratories in which a large proportion of work is performed under chemical ionization (CI) conditions, obtaining an electron impact spectrum for confirmation of the identity of an unknown may require retuning of an instrument or, perhaps, a change or cleaning of the ion source. A CI reaction scheme which would produce sufficient fragmentation with ionization of the sample to produce a mass spectrum which resembles an EI mass spectrum would allow the use of the library search routines on CI spectra of unknowns, while eliminating time-consuming alteration of the instrument.

One class of ion–neutral interactions which can occur in a CI source, producing ionization and fragmentation of the target molecule without the formation of pseudo-molecular ions (e.g., MH^+), is charge exchange. Reports of such reactions in high-pressure chemical ionization sources in analytical studies have appeared in the literature (*1*). The energetics of sample ion formation in chemical ionization sources have also been investigated by using these reactions (*2–4*). The deliberate use of charge exchange reactions in analytical mass spectrometry to study compounds of environmental interest has been reported by Hites and co-workers (*5*).

Charge exchange reactions at low pressure have been pursued extensively in an effort to understand the mechanisms by which the process takes place. Elucidation of the states in which the products are formed and, in the case of a polyatomic target, the extent of the fragmentation which may accompany the charge exchange have also been studied extensively. Several excellent reviews summarize the results of many studies (*6–9*).

Charge exchange reactions can be represented by the equation

$$X^+ + M \rightarrow X + M^+ \qquad (1)$$

where X is usually an atomic or diatomic ion of known recombination energy (RE) and M is a polyatomic neutral molecule with an appearance potential (AP) which may or may not be known. If the reaction is slightly exoergic (RE > AP), M^+ may be formed with enough internal energy to fragment. As Lindholm has shown for a large number of systems, the extent of the fragmentation is related to the magnitude of the excess energy, ΔE, deposited in M during charge exchange. Thus, the selection of a particular reagent ion to react with a given target predetermines the amount of energy which can be deposited in M^+ and thus the amount of fragmentation which can accompany ionization at a given kinetic energy (*9*).

The present study employs charge exchange reactions in the CI source to simulate the ionization and fragmentation of target molecules which occur under EI conditions. Since the ions formed during electron impact ionization are formed with a large distribution of internal energies (*10*, *11*), the phenomenon to be duplicated must involve not a single process but several. For CI reagent ions to produce from M the diverse fragment ions found in EI spectra, several fragmentation pathways must be available. The multiplicity of closely spaced states in large organic molecules renders this requirement easily met if a small amount of excess energy is available in the charge exchange process ($\Delta E > 0$). In addition, the formation of excited metastable neutrals in the reagent plasma may also provide Penning ionization reaction channels (*12*)

$$X^* + M \rightarrow X + M^+ + e^- \qquad (2)$$

The reagent gases examined were chosen so as to provide these channels in reactions with organic molecules targeted by the Environmental Protection Agency (EPA) as priority pollutants. The analytical utility of the reactions of any gas or mixture of gases with the target molecules was evaluated in terms of the ability of that reagent gas plasma to produce a mass spectrum which could be identified by a commercial data system library search using EI spectra in its library.

EXPERIMENTAL SECTION

The experiments were carried out on a modified Finnigan 3300 quadrupole mass spectrometer (*13*) using the standard chemical ionization source. The source temperature was typically maintained at 125 °C. Apparent source pressures varied between 150 and 600 mtorr, measured by a thermocouple gauge attached to the source. Since the reading indicated by a thermocouple gauge is dependent on the thermal conductivity of the gas being measured, no fixed value of pressure for all gases was chosen. Rather, the pressure was chosen to maximize the reagent ion signal of choice, which was also found to maximize the sample ion current. Thus, an optimum pressure could be established for each gas and then used for an entire series of experiments. For N_2 and CO, this pressure was 180 mtorr; for CS_2, 150 mtorr. Subsequent measurements using a capacitance manometer (MKS Model 221) showed that these pressures were roughly equivalent to the 500 mtorr thermocouple gauge reading obtained for CH_4 which optimizes sample ion production in CH_4/CI experiments in this source. Tuning of the instrument for CI was performed with CH_4 and perfluorotributylamine.

The reagent gases were obtained from Matheson Scientific (N_2 and CO) and from Aldrich (CS_2). Only in carbon monoxide was water found to be a substantial contaminant. To minimize the contribution of water to the reagent gas plasma, the gas line was passed through an 2-propanol/dry ice bath when carbon monoxide was in use. All other gases were used as received. Samples of priority pollutants were obtained from the Environmental Pro-

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Table I. Compounds Targeted by the EPA as Priority Pollutants Used in This Study

base neutrals	phthalates	chlorobenzenes	phenols	pesticides
acenaphthene	dimethyl	*o*-dichloro-	phenol	aldrin
acenaphthalene	diethyl	*m*-dichloro-	*o*-chloro-	chlordane
anthracene	dibutyl	*p*-dichloro-	2,4-dichloro-	DDE-*p,p'*
fluoranthene	dioctyl	trichloro-	2,4,6-trichloro-	DDT
fluorene			pentachloro-	
naphthalene			*o*-nitro-	
phenanthrene			*p*-nitro-	
pyrene			dimethyl-	

Table II. Reagent Ions for Charge Exchange

ions	recombination energies, eV (*14*)	Penning ionization states, eV
N_2^+	15.58	6.16, 8.54 (*15*)
		11.1 (*16*)
CO^+	14.01	6.01 (*15*)
CS_2^+	10.08	5.3, 6.8, 9.8 (*17*)

tection Agency and were used without further purification.

Samples were introduced to the ion source directly from the solids probe, as well as from the gas chromatograph. A 6-ft SP 2250 packed column was coupled to the mass spectrometer by means of a glass jet separator. Helium carrier gas was used throughout all the GC experiments. The reagent gas of choice was introduced through the solids probe inlet. No particular effort was made to explore the lower limits of detection; sensitivities appear to be similar to those of methane chemical ionization.

RESULTS AND DISCUSSION

The sample species examined in this study constitute five different categories of priority pollutants and aromatic compounds, as shown in Table I. Most of their appearance potentials lie between 8 and 9 eV (*14*). Table II lists the reagent ions employed, together with their recombination energies (*14*) and Penning ionization states (*15–17*). Comparison of the recombination energies with the 8 to 9 eV appearance potentials suggests that the charge exchange reactions between each of the reagent ions and the target molecules are exoergic. These numbers also suggest that for reactions of N_2 and CS_2 with these targets Penning ionization may compete with charge exchange.

The degree of fragmentation accompanying charge exchange in these reactions is determined by two factors: the strength of the bonds in the sample molecule and the amount of excess energy available to break them. Bond strengths are characteristic of classes of molecules and thus are similar for similar species. ΔE is fixed by the difference between the recombination energy of the reagent ion and the appearance potential of the simple molecule. If $\Delta E > 0$, M^+ will be formed in an excited state. Dissociation of M^+ may follow as a result of that excitation, depending on the fragmentation pathways available at that internal energy ΔE and the amount of collisional stabilization that may occur in the chemical ionization source.

Under electron impact conditions, a population of electrons of a given nominal energy collides with target molecules. These collisions will form sample ions with differing amounts of internal excitation, depending on the dynamics of the particular collision which forms a given M^+. A population of target ions will be formed, having a distribution of internal energies. Fragmentation of $(M^+)^*$ will be governed by the magnitude of the excitation and the strength of its bonds. Thus an EI spectrum may or may not contain molecular ions; may or may not contain fragment ions.

Reaction energetics to illustrate such differences are shown in Table III, using phenanthrene and chlorobenzene as examples. The difference in appearance potentials between the two species is only about 1 eV. The appearance potentials of the most easily formed fragment ions for the two are considerably different: for phenanthrene, loss of a hydrogen or of acetylene requires an excess energy of 8 eV, while a chlorine can be lost from chlorobenzene with an excess energy of only about 3 eV. Since the distribution of energies with which M^+ is formed favors the lower energy fragmentations, the high-energy fragmentation processes either do not occur or occur with low probability. The EI mass spectra of very stable compounds like phenanthrene are dominated by molecular ions, while the EI mass spectra of compounds with weaker bonds, such as chlorobenzene, contain many characteristic fragment ions.

Table III. Energetics of Fragmentation

molecule	ion formed	loss	appearance potential, eV (*14*)
phenanthrene	$C_{14}H_{10}^+$	e^-	7.8
$C_{14}H_{10}$	$C_{14}H_9^+$	H	16.2
	$C_{12}H_8^+$	C_2H_2	16.6
	$C_{14}H_8^+$	H_2	18.6
	$C_{14}H_7^+$	H_2 + H	20.0
chlorobenzene	$C_6H_5Cl^+$	e^-	9.0
C_6H_5Cl	$C_6H_5^+$	Cl	12.6
	$C_6H_4^+$	HCl	14.9

Similar considerations hold for the fragmentation of M^+ formed by charge exchange with the several reagent gases examined. Differences in the relative intensities of fragment ions found in charge exchange spectra of a particular target with different reagent gases can be attributed to both the magnitude of ΔE and the energetics of the process required to produce fragmentation.

For the polynuclear aromatic hydrocarbons (PAH), charge exchange spectra are dominated by molecular ions. Table IV tabulates the percent relative abundances of the N_2 charge exchange spectra for these species, along with tabulations of the percent relative abundances from their EI spectra. While some differences in relative intensity were observed, in general the charge exchange spectra show remarkable similarity to EI spectra. As expected, reactions of CO^+ and CS_2^+ with these targets produced even less fragmentation.

The spectra of the substituted benzenes, by contrast, prove very sensitive to the amount of energy available with a particular reagent gas. The charge exchange spectra of dichlorobenzene, shown in Figure 1, indicate the differences in fragmentation which result from differences in ΔE. Reactions with N_2^+ result almost entirely in formation of m/e 111, loss of Cl. With CO^+ dichlorobenzene forms predominantly $(M - Cl)^+$ ions, but the spectra also contain some M^+ (m/e 146) and $(M - Cl - HCl)^+$ (m/e 75) ions. CS_2^+ produces almost entirely molecular ions. Inspection of the EI spectrum, shown in Figure 2, shows that the same fragmentations are produced by EI ionization, but they occur with different probabilities. The use of a mixture of reagent gases can alter those proba-

Table IV. Comparison of NBS EI Library Spectra with N_2^+ Charge Transfer CI Spectra[a]

Naphthalene														
m/e	129	128	127	126	102	78	77	75	74	64	63	51	50	
NBS	6	58	6	4	5		3	2	2	4	3	5	2	
N_2 C.T.	5	51	11		20	8				2	3			
Acenaphthalene														
m/e	154	153	152	151	150	76	75	74	63	62				
NBS	2	8	53	9	6	9	8			5				
N_2 C.T.		8	65	6		6	3	3	6	3				
Acenaphthene														
m/e	155	154	153	152	151	150	77	76	75	74	63	51		
NBS	4	31	27	13	4	2	3	7	2	2	3	2		
N_2 C.T.		22	55	7			3	8			5			
Fluorene														
m/e	167	166	165	164	163	87	86	83	82	75	74	69	63	62
NBS	5	38	30	3	4	2	2	5	4	2			3	
N_2 C.T.	2	22	52					5	7	2		3	5	2
Anthracene														
m/e	179	178	176	175	152	151	150	89	87	76	75	74	63	62
NBS	6	41	7	2	3	3	2	8	2	6	3	2	3	2
N_2 C.T.	8	56			4				3	9	5	4	6	5
Phenanthrene														
m/e	179	178	177	176	152	151	150	89	88	87	76	75	74	63	62
NBS	6	43	3	6	4	3	2	8	6	2	9	3	2	3	
N_2 C.T.	6	43	6		9			7	5		9	3	3	6	3
Fluoranthene														
m/e	203	202	201	200	199	101	100	88	87	75	74	63	62	
NBS	10	52	6	9	2	7	4	2	3	2	3			
N_2 C.T.	10	63				7	6	3		3	3	3	2	
Pyrene														
m/e	203	202	201	200	199	101	100	88	87	75				
NBS	12	49	10	10	2	7	4	3	3					
N_2 C.T.	10	66				11	6	4		3				

[a] Values given as percent relative abundance.

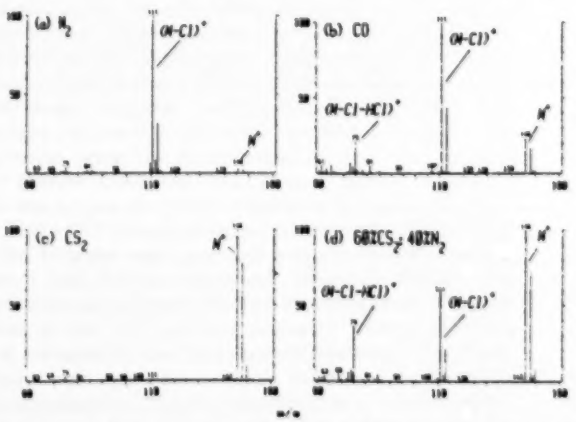

Figure 1. Charge exchange mass spectra of dichlorobenzene with four reagent ions.

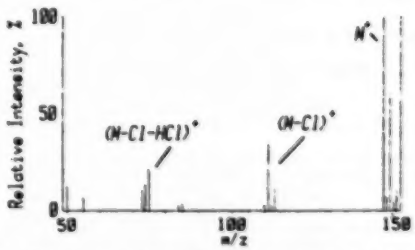

Figure 2. NBS electron impact library spectrum of dichlorobenzene.

bilities sufficiently to alter the relative intensities of ions in the charge exchange spectrum. The spectrum of a 60:40 mixture of CS_2 and N_2 is also shown in Figure 1. Similarity to the EI spectrum is obvious. Thus, tailoring the reagent gas mixture to suit a compound can in many cases result in a charge exchange spectrum that is virtually identical to the EI spectrum of a particular compound.

For analytical survey purposes, however, such fine tuning is not only impractical but in fact subverts the goal of providing a general technique for characterizing samples of unknowns rapidly. Producing spectra that are visually similar is one means of making comparisons of the efficacy of a particular reaction scheme. Ultimately, the goal is to produce charge exchange spectra which a computer search routine deems similar to EI spectra stored in computer libraries.

Table V. Computer Assessment of Similarity between CO^+ Charge Transfer CI Spectra and NBS EI Library Spectra

priority pollutant	purity	fit	rfit
methyl phthalate	878	900	967
ethyl phthalate	883	902	918
butyl phthalate	857	867	968
octyl phthalate	574	754	731
o-dichlorobenzene	870	952	910
m-dichlorobenzene	913	995	913
p-dichlorobenzene	847	926	904
1,2,4-trichlorobenzene	853	937	901
phenol	749	809	749
o-chlorophenol	841	930	848
2,4-dichlorophenol	498	593	544
2,4,6-trichlorophenol	627	658	815
2,4,5-trichlorophenol	494	589	693
pentachlorophenol	574	695	599
o-nitrophenol	522	593	522
chlorocresol	782	905	725
BHC	574	745	604
DDT	556	771	705

The library search routine employed in these studies, available as part of the Incos Data System, reports similarity between the spectrum of an unknown and that of a given library entry in terms of three parameters: purity, fit, and rfit. Purity indicates the resemblance of the unknown spectrum to that of a given library entry. Fit shows the similarity of the library spectrum to that of the unknown, excluding peaks of the unknown not present in the library entry. Rfit looks for those compounds in the library spectra which may be included in the unknown spectra. This reverse search method is useful for the elucidation of mixture spectra. The values of these parameters range from 0 to 1000, with 1000 indicating a perfect match, both in peaks identified and in relative intensities. In general, values of 800–900 indicate good matches; values of 600–800 indicate similarities in the spectra of the unknown and the library entry. Purities and fits greater than 800 indicate sufficiently good matches that the library spectra flagged by the search should be considered seriously; values above 600 indicate spectra which may suggest the class of compound to which the unknown belongs, if not its precise identity.

A correct match for the compound being studied was included among the list of the five best matches in the library searches of the charge exchange spectra of virtually all the samples with all the reagent gases. Fine tuning of the reagent gas plasma could produce spectra which matched to purities and fits greater than 900. As indicated previously, however, a more general reaction scheme is desirable for survey analytical work. From the studies reported here, the reactions of CO^+ provide such a tool. In all cases examined, the correct species was among the first five listed by the computer when it searched a CO^+ charge exchange spectrum against the NBS libraries. In many cases, matches with purity and fit values of greater than 800 were obtained. Shown in Table V is a representative sampling of the identifications made in library searches of the CO^+/priority pollutant charge exchange spectra. As noted in the Experimental Section of this paper, the quadrupole mass spectrometer was tuned for optimum chemical ionization. Greater resemblance in relative abundances between these quadrupole CI spectra and the (in general) magnetic sector EI spectra might well be obtained by employing the standard ion abundance calibration suggested by Eichelberger (*18*).

CONCLUSIONS

The goal of library searches is to put in the hands of the operator the library spectra which most clearly resemble the spectrum of the unknown, according to the algorithm employed by the computer for library searching. Positive identification of unknowns cannot, of course, be made without additional information: GC retention times and accurate mass measurements, for example. The speed of the process can be considerably enhanced, however, if the operator has at his disposal the identification available from preliminary screenings. For laboratories engaged primarily in chemical ionization studies, the charge exchange reactions of CO^+ can provide the EI-like spectra necessary for computer-generated searches of NBS library spectra. Visual inspection of the matching spectra listed by the computer can suggest to the operator the next avenue to pursue.

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Registry No. BHC, 58-89-9; DDT, 50-29-3; naphthalene, 91-20-3; acenaphthalene, 208-96-8; acenaphthene, 83-32-9; fluorene, 86-73-7; anthracene, 120-12-7; phenanthrene, 85-01-8; fluoranthene, 206-44-0; pyrene, 129-00-0; dimethyl phthalate, 131-11-3; diethyl phthalate, 84-66-2; dibutyl phthalate, 84-74-2; dioctyl phthalate, 117-84-0; *o*-dichlorobenzene, 95-50-1; *m*-dichlorobenzene, 541-73-1; *p*-dichlorobenzene, 106-46-7; 1,2,4-trichlorobenzene, 120-82-1; phenol, 108-95-2; *o*-chlorophenol, 95-57-8; 2,4-dichlorophenol, 120-83-2; 2,4,6-trichlorophenol, 88-06-2; 2,4,5-trichlorophenol, 95-95-4; pentachlorophenol, 87-86-5; *o*-nitrophenol, 88-75-5; chlorocresol, 1321-10-4.

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